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# Adsorption property and inhibition of Stainless Steel 304 corrosion in hydrochloric acid media by water-soluble amoxicillin drug

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Abstract: Corrosion inhibition of SS 304 in 2 mol L-1 HCl by amoxicillin drug in the concentration range of 50-300 ppm has been studied using weight loss (WL), potentiodynamic polarization (PP); electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. All experiments showed that the inhibition efficiency (IE %) increased with amoxicillin concentrations and decreased by raising the temperature. PP curves indicated that amoxicillin acted as a mixed-type inhibitor. The absorption of drug molecule on the SS 304 surface was confirmed by atomic force microscopy (AFM) and Fourier transform infrared (FTIR) spectroscopy and found to follow Langmuir adsorption isotherm. The results obtained from chemical and electrochemical techniques are in good covenant. All the experimental results concluded that amoxicillin acted as good corrosion inhibitor

Keywords: Corrosion inhibition, SS 304, HCl, EIS, FTIR, AFM

## 1. INTRODUCTION

Stainless steel materials have high corrosion resistance capacity because of the presence of chromium, which forms a passive film layer of chromium-rich oxide in the presence of oxygen at lower temperatures; this forms a barrier with its surroundings<sup>1,2</sup>. However, this layer could be damaged in harsh environments.

Corrosion inhibitors are added to reduce the rate at which this layer is deteriorated in different media. In acidic media, heterocyclic corrosion inhibitors such as organic compounds containing nitrogen, sulfur, and oxygen and their derivatives, are the most effective inhibitors<sup>3</sup>. The efficiency of organic compounds to act as inhibitors is due to the formation of an organic film layer on a metal surface <sup>4</sup>. Organic heterocyclic compounds have been used for the corrosion inhibition of C-steel<sup>5-11</sup>, Cu<sup>12</sup>, Al<sup>13-15</sup> and other metals<sup>16</sup> in different aqueous medium. Adsorption of the drug facilitated to protect the metal surface<sup>17</sup>.

A few medications such as tetracycline, cloxcillin, azithromycin, ampiclox, ampicillin and orphenadrine have been discovered great inhibition for corrosion of metal surface. The select of some medication for inhibitor of corrosion is taking in the following:

- 1. drug molecules contain oxygen, sulphur and nitrogen as active sites,
- 2. it is environmentally friendly furthermore vital in organic responses and
- 3. Drugs can be easily produced and purified<sup>18</sup>.

In recent years the drugs used as corrosion inhibitors for various metals result to their nontoxic nature <sup>19, 20</sup>. Adsorption of the drug molecules on the metal surface facilitates its inhibition <sup>21</sup>. A few medications have been discovered to be great corrosion inhibitors for metals such as: Biopolymer gave 86 % IE for Cu in NaCl<sup>22</sup>, pyromellitic diimide linked to oxadiazole cycle gave 84.6 % IE for CS in HCl<sup>23</sup>, 2-mercaptobenzimidazole gave 82% IE for CS in HCl<sup>24</sup>.

Antidiabetic drug Janumet gave 88.7% IE for MS in HCl<sup>25</sup>, Januvia gave 79.5% IE for Zn in HCl<sup>26</sup>, Cefuroxime Axetil gave 89.9% IE for Al in HCl<sup>27</sup>, Phenytoin sodium gave 79% for CS in HCl<sup>28</sup>, Aspirin gave 71% IE for MS in H<sub>2</sub>SO<sub>4</sub> <sup>29</sup>, Septazole gave 84.8% IE for Cu in HCl <sup>30</sup> and Chloroquine diphosphate gave 80% IE for mild steel in HCl <sup>31</sup>. Ospamox under the name of amoxicillin is used an antibiotic useful for the treatment of a number of bacterial infections, treatment for middle ear infections, it may also be used for strep throat, pneumonia, skin infections, and urinary tract infections among others <sup>32</sup>.

The objective of this study is to investigate the inhibitive behavior of amoxicillin drug towards the corrosion of SS 304 in 2M HCl using chemical and electrochemical techniques. The surface morphology of the SS 304 specimens was also analyzed.

#### 2- EXPERIMENTAL DETAIL

2. 1- Metal sample: The composition of metal sample in weight % is: C 0.08, Si 0.75, Mn 2, Cr 18-20, P 0.045, Ni 10.5 and Fe the rest

#### 2.2 - Chemicals

**2.2.1-** *Inhibitor:* Amoxicillin is the investigated drug which has been used as inhibitor and purchased from Sandozinc and Pfizer inc companies and used as received.

(2S, 5R, 6R)-6-{[(2R)-2-amino-2-(4-hydroxyphenyl)-acetyl] amino}-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-24-carboxylic acid

Mol. Formula =  $C_{16}H_{19}N_3O_5S$ , Mol. Weight =365.4 g/mol

**2.2.2-** *Solutions:* The aggressive solutions, 2M HCl was prepared by dilution of analytical grade (%37) HCl with bidistilled water. The concentration range of the inhibitor, which used was between 50 and 300 ppm

#### 2.3- Methods used for corrosion techniques

2.3.1. Weight loss (WL) technique: For WL measurements, square specimens of surface area 2 x 2 x 2 cm which exposed to the corrosive medium that used. The specimens were abraded with emery paper grit sizes (400,800 and 1200) and clean with acetone. Then rinsed several times with bi-distilled water, and finally dried by filter papers. The WL measurements were carried out in a 100 ml glass beaker placed in a water thermostat. The specimens were then immediately immersed in the test solution without and with different concentrations of the investigated drug. All aggressive acid solutions were opened to the air. After three hours, the specimens were taken out, washed, dried, and weighted accurately per thirty minutes. The average WL for seven square SS 304 specimens will be obtained. The IE % and the  $(\theta)$  of amoxicillin drug for the corrosion of SS 304 were calculated as follows<sup>33</sup>:

% IE = 
$$\theta \times 100 = [1 - (W/W^{\circ})] \times 100$$
 (1)

Where, W° and W are the WL's, without and with adding various concentrations of investigated inhibitor respectively.

2.3.2- Potentiodynamic polarization (PP) technique: PP experiments were carried out in a classical three-electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode. The working electrode was in the form of a square cut from SS 304 sheet fixed in epoxy resin of poly tetrafluoroethylene so that the flat surface area was 1.0 cm<sup>2</sup>. The working electrode was polisher with emery paper grit 1200 in size. Before measurement, the electrode was immersed in solution at the natural potential for 30 min until a steady state was reached. All experiments were carried out in freshly prepared solutions at room temperature and results were always repeated at least three times to check the validity of the results. Calculation of % IE and the  $\theta$  as below<sup>34</sup>:

IE % = 
$$\theta$$
 x 100 =  $\left[1 - \left(i_{\text{corr(inh)}} / i_{\text{corr(free)}}\right)\right] \times 100$  (2)

Where  $i_{corr(free)}$  and  $i_{corr(inh)}$  are the corrosion current densities in the absence and presence of drug, respectively.

2.3.3- Electrochemical impedance spectroscopy (EIS) technique: All EIS measurements were performed at open circuit potential  $E_{ocp}$  at  $25\pm1^{\circ}C$  over a wide frequency range of  $(1x10^{5} \text{ Hz to } x\ 0.1 \text{ Hz})$ . The obtained diameters of the capacitive loops increase in presence of drug, and are indicated of the capacity of the extent of inhibition of corrosion process, contrary to the decrease of the capacity of double layer  $(C_{dl})$  which is defined as:

$$C_{dl} = 1/(2 \pi f_{max} R_p)$$
 (3)

Where  $f_{\text{max}}$  is the maximum frequency. The IE and the  $\theta$  obtained from the impedance measurements were defined by the following relation:

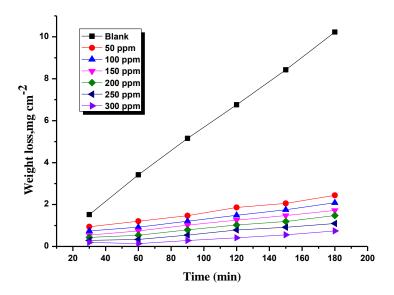
IE % = 
$$\theta \times 100 = [1 - (R_p^0/R_p)] \times 100$$
 (4)

Where,  $R_p^0$  and  $R_p$  are the charge transfer resistance in the absence and presence of inhibitor, respectively.

- 2.3.4. Electrochemical frequency modulation (EFM) technique: EFM experiments were performed by applying a potential perturbation signal with abundance 10 mV with two sine waves of 2 and 5 Hz. The choice for the frequencies of 2 and 5Hz was based on three arguments<sup>35</sup>. The larger peaks were used to calculate the corrosion current density ( $i_{corr}$ ), the Tafel slopes ( $\beta_c$  and  $\beta_a$ ) and the causality factors<sup>36</sup> CF<sub>2</sub> and CF<sub>3</sub>. The % IE<sub>EFM</sub> was calculated as in Eq. 2
- All electrochemical experiments were carried out using Gamry instrument PCI300/4 Potentiostat/Galvanostat/Zra analyzer, DC105 Corrosion software, EIS300 Electrochemical Impedance Spectroscopy software, EFM140 Electrochemical Frequency Modulation software and Echem Analyst 5.5 for results plotting, graphing, data fitting and calculating.
- 2. 3.5- Surface Examinations: The SS 304 specimens used for analysis of morphology surface were prepared in 2M HCl acid (blank) and with 300 ppm of Amoxicillin at room temperature for one day after abraded mechanically using different emery papers up to 1200 grit size. Then, after this immersion time, the specimens were cleaned gently with bi-distilled water, carefully dried and mounted into the performed specimens examined by using Fourier transform infrared spectroscopy (FTIR) and atomic force microscope (AFM).

#### 3- RESULTS AND DISCUSSION

3.1. Weight loss measurement: Weight loss of SS 304, in mg cm<sup>-2</sup> of the surface area, was determined at various time periods in the absence and presence of different concentrations (50 -300 ppm) of amoxicillin. The curves obtained in the presence of different concentrations of drug fall significantly below that of free acid as shown in **Figure-1**. The % IE's are listed in **Table-1**. In all cases, the efficiency of the drug increases with increasing concentration of the drug, but the rate of corrosion was decreased. These results indicated that, amoxicillin under study are good efficient as an inhibitor for SS 304 dissolved in HCl solution.



**Figure 1**: Weight loss-time curves for the dissolution of SS 304 in the absence and presence of different concentrations of Amoxicillin at 25°C

**Table 1:** Variation of % IE of the drug with its molar concentrations at 25°C from weight loss measurements at 120 min immersion in 2 M HCl

Conc., ppm	k <sub>corr.</sub> mg cm <sup>-2</sup> min <sup>-1</sup>	IE%
Blank	0.046	
50	0.0092	80.1
100	0.0082	82.2
150	0.0075	83.8
200	0.0063	86.3
250	0.0054	88.2
300	0.0045	90.1

**3.1.1.** *Effect of temperature:* Corrosion reactions are usually regarded as Arrhenius processes and the rate constant ( $k_{corr}$ ) can be expressed by the relation:

$$\text{Log } k_{\text{corr.}} = A - (E_a^*/2.303RT)$$
 (5)

where,  $E_a^*$  is the activation energy of the corrosion process, R is the universal gas constant, T is the absolute temperature and A is a Arrhenius pre-exponential constant depends on the metal type and electrolyte. Arrhenius plots of log  $k_{corr}$  vs (1/T) for SS 304 in 2M HCl in the absence and presence of different concentrations of amoxicillin is shown graphically in **Figure-2**. The variation of log  $k_{corr}$  vs (1/T) is a linear one and the values of  $E_a^*$  are obtained and summarized in **Table -2**.

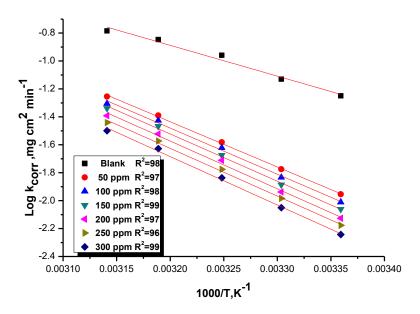
**Table 2:** Thermodynamic activation parameters for the dissolution of SS 304 in 2M HCl in the absence and presence of different concentrations of investigated drug

Conc.	Activation parameters				
	$\mathbf{E}^*_{a}$	$\Delta  ext{H}^*$	$-\Delta S^*$ J mol $^{-1}$ K $^{-1}$		
ppm	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>		
Blank	48.2	45.5	119		
50	63.6	65.8	72.6		
100	65.3	67.4	66.2		
150	66.1	69.3	64.2		
200	69.2	71.5	58.2		
250	70.5	72.9	52.5		
300	72.2	74.9	50.6		

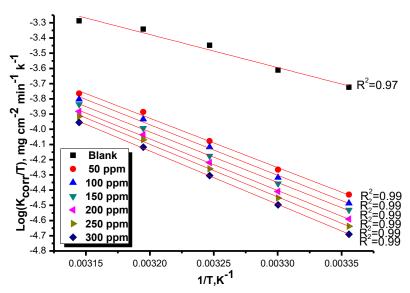
The increase in  $E_a^*$  with the addition of different concentrations of the drug, indicating that, the energy barrier for the corrosion reaction increased. It is also indicated that the whole process is controlled by surface reaction, since the activation energy of the corrosion process<sup>37</sup> is over 20 kJ mol<sup>-1</sup>. Enthalpy and entropy of activation ( $\Delta H^*$ ,  $\Delta S^*$ ) are calculated from transition state theory using the following equation<sup>38</sup>.

$$k_{corr.} = (RT/Nh) \exp(\Delta S^*/R) \exp(\Delta H^*/RT)$$
 (6)

Where, h is Planck's constant, N is Avogadro's number. A plot of log ( $k_{corr.}/T$ ) vs. (1/T) also gave straight lines as shown in **Figure-3**, for SS 304 dissolution in 2M HCl in the absence and presence of different concentrations of amoxicillin. The slopes of these lines equal- $\Delta H^*/2.303R$  and the intercept equal log [RT/Nh] + ( $\Delta S^*/2.303R$ ), that the value of  $\Delta H^*$  and  $\Delta S^*$  were calculated and listed in **Table 2**. From these results, it is clear that the presence of the tested drug increased the  $E^*_a$  values and consequently decreased the rate of corrosion of the SS 304.



**Figure 2:** Arrhenius plots (log  $k_{corr}$  vs. 1/T) for corrosion of SS 304 in 2M HCl in the absence and presence of different concentrations of amoxicillin drug



**Figure 3:** Plots of (log  $k_{corr.}$  / T) vs. (1/ T) for corrosion of SS 304 in 2M HCl in the absence and presence of different concentrations of amoxicillin at 25°C

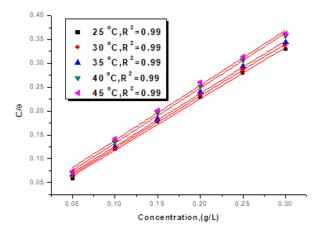
These results indicated that the tested drug acted as inhibitors through increasing  $E_a^*$  of SS 304 dissolution by making a barrier to mass and charge transfer by their adsorption on the SS 304 surface. The values of  $\Delta S^*$  reflect the strong adsorption of this drug on the SS 304 surface. The values of  $\Delta S^*$  in the absence and presence of the tested drug are large and negative; this indicates that the activated complex in the rate-determining step represents an association rather than dissociation step, meaning that a decreases in disordering takes place on going from reactants to the activated complex and the activated molecules were in a higher order state than that at the initial state<sup>39</sup>.

**3.1.2.** Adsorption isotherm: Assuming the corrosion inhibition due to by the adsorption of Amoxicillin, and the values of the degree of surface coverage for the different concentrations of the drug in 2M HCl were evaluated from weight loss measured using equation (1)

From the values of  $(\Theta)$ , it is obvious that the values of  $(\Theta)$  increased with increasing the concentration of Amoxicillin. By using these values of surface coverage, for applying different adsorption isotherms to obey with experimental data. Langmuir adsorption isotherm was found to fit the experimental data. The mathematical expression of Langmuir is given as follows<sup>40</sup>.

$$C/\Theta = 1/k_{ads} + C \tag{7}$$

Where,  $k_{ads}$  is the adsorption equilibrium constant. Plotting (C/ $\Theta$ ) versus (C) of Amoxicillin at various temperatures is shown in **Figure-4**, recommends that no force repulsion or attraction between the atoms adsorbed, ever after relationship a linear is given with, intercept equal to  $(1/k_{ads})$  and slope similar the unity, the adsorption constant being result to the standard free energy of  $\Delta G^o_{ads}$  by the following relation:



**Figure 4:** Langmuir adsorption isotherm plotted as (log C) vs  $(C/\theta)$  of the investigated drug for corrosion of SS 304 in 2M HCl solution

$$\Delta G^{o}_{ads} = -RT \ln (55.5 K_{ads}) \tag{8}$$

Where, R is the universal gas constant, T is the absolute temperature and 55.5 is the concentration of water in the solution in M/L. The  $\Delta G^o_{ads}$  values at all studied at different temperatures which calculated by the above equation (13) and recorded in **Table-3**. The heat of adsorption ( $\Delta H^o_{ads.}$ ) was calculated according to the Van't Hoff equation<sup>41</sup>.

$$Log k_{ads} = (-\Delta H^{\circ}_{ads} / 2.303RT) + constant$$
 (9)

Plotting (log  $K_{ads.}$ ) against (1/T) give straight line that shown in **Figure- 5**, the straight line gives slope equal  $(\Delta H^o_{ads.}/2.303R)$ , from this slope, and the  $\Delta H^o_{ads}$  were calculated and listed in **Table- 3**. Then by apply the following equation:

$$\Delta G^{o}_{ads} = \Delta H^{o}_{ads.} - T\Delta S^{o}_{ads.} \tag{10}$$

From introducing the values of  $\Delta G^o_{ads}$  and  $\Delta H^o_{ads}$ , the  $\Delta S^o_{ads}$  was calculated at all studied temperatures by the above equation (15). All thermodynamic adsorption parameters for Amoxicillin inhibitor on SS 304 from 2M HCl solution can be concluded that:

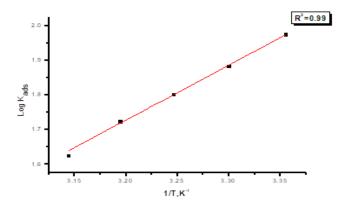
- 1. The experimental data give good curves fitting for the applied adsorption isotherms as the correlation coefficients were in the range (0.99 0.98)
- 2. K<sub>ads.</sub> values increases with increasing temperatures from 25 to 45°C
- 3. The negative values of  $\Delta G^o_{ads}$  reflected that the adsorption of Amoxicillin on SS 304 surface in 2M HCl solution is spontaneous process
- 4. ΔG°<sub>ads</sub> slightly increases (becomes less negative) with increasing temperatures which indicated the occurrence of endothermic process and the adsorption was unfavorable with increasing reaction temperature as a result of the inhibitor desorption from the steel surface<sup>42</sup>
- 5. The value of  $\Delta G^{o}_{ads}$  around -20 kJ mol<sup>-1</sup> or lower indicates the electrostatic interaction between charged metal surface and charge organic molecules in the bulk of the solution i.e. physisorption

6. The negative sign of  $\Delta H^o_{ads}$  refer to the adsorption of inhibitor molecules is an exothermic process, indicating that the adsorption is physical adsorption. The unshared electron pairs in investigate molecule may attractive with positive center on the surface of SS 304 by electrostatic attraction to provide a protective film prevent corrosion process<sup>43</sup>

7. The values of  $\Delta S^o_{ads}$  in the presence of investigate inhibitor are small and negative that is accompanied with endothermic adsorption process<sup>44</sup>

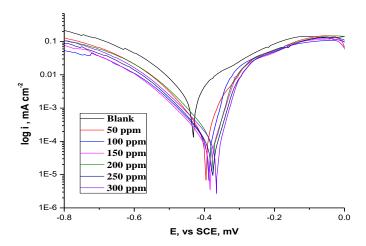
<b>Table 3:</b> Equilibrium constant ( $K_{ads}$ ), adsorption free energy ( $\Delta G^{\circ}_{ads}$ ) for the adsorption of
drug on SS 304 in 2M HCl.

Temp.°C	$egin{array}{c} K_{ads} \ M^{-1} \end{array}$	-∆G° <sub>ads</sub> kJ mol <sup>-1</sup>	-∆H° <sub>ads</sub> kJ mol <sup>-1</sup>	$-\Delta S^{o}_{ads}$ J mol <sup>-1</sup> K <sup>-1</sup>
25	186	21.9	33	73.2
30	159	21.2		71.3
35	139	20.7		69.9
40	110	20.1		68.6
45	88	19.9		66.4



**Figure 5:** (log k<sub>ads</sub>) vs (1000/T) for the corrosion of SS 304 in 2M HCl in the presence of Amoxicillin at different temperatures.

3.2- Potentiodynamic polarization: Anodic and cathodic polarizations were carried out potentiodynamic in 2M HCl solution in the absence and presence of various concentrations of Amoxicillin at  $25^{\circ}$ C. The results are drawing in **Figure -6**. The obtained potentiodynamic polarization parameters are listed in **Table-4**. These results indicate that the cathodic and anodic curves obtained according to Tafel-type behavior. The form of the curves is very similar either in the cathodic or in the anodic side, which indicates that the mechanisms of SS 304 dissolution and hydrogen reduction apparently remain in the presence of the inhibitor. The addition of Amoxicillin decreased both the cathodic and anodic current densities and caused mainly parallel displacement to the more negative and positive values, respectively, i.e. the presence of Amoxicillin in solution inhibit both the hydrogen evolution and the anodic dissolution processes with the overall shift of  $E_{corr}$  to slightly less negative values.



**Figure 6**: Potentiodynamic polarization curves for the corrosion of SS 304 in 2M HCl in the absence and presence of various concentrations of amoxicillin at 25°C

**Table 4:** The effect of concentration of amoxicillin on the free corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), Tafel slopes ( $\beta_a$ &  $\beta_c$ ), % IE, and ( $\Theta$ ) for the corrosion of SS 304 in 2M HCl at 25°C

Conc.	i <sub>corr</sub>	-E <sub>corr.</sub>	$\beta_a$	-β <sub>c</sub>	CR	Θ	% IE
ppm	mA/cm <sup>-2</sup>	mV(SCE)	mV dec-1	mV dec <sup>-1</sup>	mpy		
0.0	995	433	120	151	390		
50	165	419	115	154	251	0.834	83.4
100	157	415	117	151	245	0.842	84.2
150	144	412	111	147	231	0.855	85.5
200	129	409	103	149	228	0.870	87.0
250	115	405	118	145	193	0.884	88.4
300	99	400	100	148	122	0.90	90.05

The results also show that the slopes of the anodic and the cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ ) was slightly changed on increasing the concentration of the tested compounds. This indicates that there is no change of the mechanism of inhibition in the presence and absence of inhibitors. This means that the Amoxicillin is a mixed type inhibitor, but the cathode is more preferentially polarized than the anode. The higher values of Tafel slope can be related to the surface kinetic process rather the diffusion-controlled process<sup>45</sup>.

The constancy and the cathodic slope obtained from the electrochemical measurements indicate that the hydrogen evolution reaction was activation controlled<sup>46</sup> and the addition of the inhibitor did not modify the mechanism of this process. This result appears that the inhibition mode of the Amoxicillin was used by

simple adheres of the surface by adsorption process.

3.3- Electrochemical impedance spectroscopy (EIS) tests: Impedance diagrams (Nyquist and bode) at frequencies ranging from 0.1 Hz to  $10^5$  Hz with 10 mV amplitude signal at OCP for SS 304 in 2M HCl in the absence and presence of different concentrations of Amoxicillin are obtained. The equivalent circuit that describe for metal and electrolyte are shown in **Figure-7**, which represents a single charge transfer reaction and fits well with our experimental results. The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit<sup>47</sup>. The double layer capacitance,  $C_{dl}$ , for a circuit including a CPE parameter ( $Y_0$  and n) were calculated<sup>48</sup> from eq.8:

$$C_{dl} = Y_0(\omega_{max})^{n-1} \tag{11}$$

where  $Y_0$  is the magnitude of the CPE,  $\omega_{max} = 2\pi f_{max}$ ,  $f_{max}$  is the frequency at which the imaginary component of the impedance is maximal and the factor n is an adjustable parameter that usually lies between 0.5 and 1.0. EIS parameters and (% IE) were calculated and recorded in **Table-5**. The obtained Nyquist and bode plotting for Amoxicillin is shown in **Figure-8**. Nyquist spectrum is characterized by a single full half-circle. This shows that the corrosion of SS 304 is controlled by a charge transfer process<sup>49</sup>. The diameters of the capacitive loop obtained increases in the presence of Amoxicillin were indicating that increasing the degree of inhibition of the corrosion process<sup>50</sup>.

It was observed from the obtained EIS data that  $R_p$  increases and  $C_{dl}$  decreases with the increasing of inhibitor concentrations. The increase in  $R_p$  values gives increasing of the inhibition efficiency, due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface to form an adhesive film on the metal surface. This suggests that the coverage of the metal surface of the film decreases the double layer thickness. Also, this decreasing of  $C_{dl}$  with increasing the inhibitor concentration can result from a decrease in local dielectric constant which indicating that, the inhibitor was adsorbed on the surface of both anodic and cathodic sites<sup>51</sup>.

Fourier transform infrared spectroscopy (FTIR)

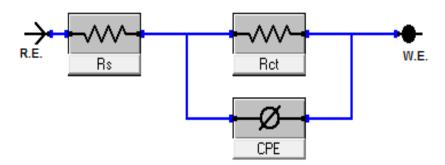
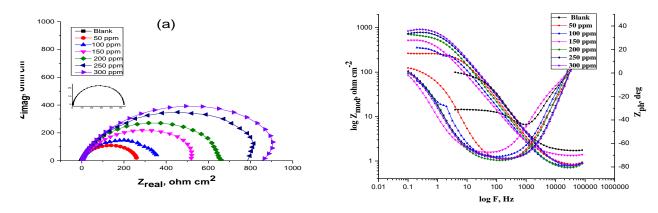


Figure 7: The electrical equivalent circuit model used to fit the experimental results



**Figure 8:** The Nyquist (a) and Bode(b) plots for corrosion of SS 304 in 2M HCl in the absence and presence of different concentrations of Amoxicillin at 25°C

**Table 5**: Electrochemical kinetic parameters obtained by EIS technique for SS 304 in M HCl without and with various concentrations of Amoxicillin at 25°C

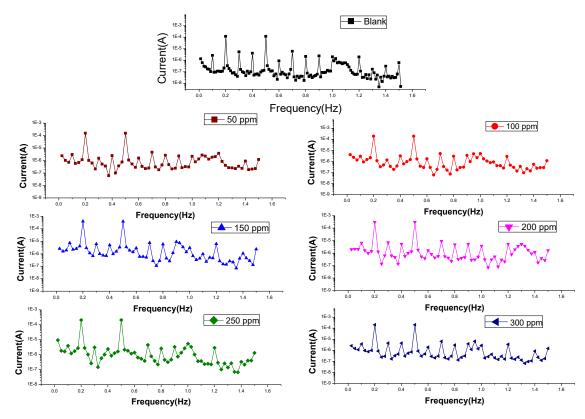
Conc.	$R_p$	C <sub>dl</sub>	Ө	% IE
ppm	$\Omega$ cm <sup>2</sup>	μF cm <sup>2</sup>		
0.0	48.9	216		
50	261	164	0.813	81.3
100	339	113	0.856	85.6
150	564	109	0.913	91.3
200	673	88	0.927	92.7
250	736	79	0.934	93.4
300	810	42	0.940	94.0

3.4- Electrochemical frequency modulation technique (EFM) tests: EFM is a nondestructive corrosion measurement technique that can directly and quickly determine the corrosion current value without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it a very good technique for determination corrosion information's<sup>52</sup>. The strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses. The EFM Intermodulation spectrums of SS 304 in 2M HCl acid solution and in 2M HCl with containing (50 – 300 ppm) of the Amoxicillin are shown in **Figure -9**. The harmonic and Inter-modulation peaks are clearly visible and are much larger than the background noise. The experimental EFM-data were treated using two different models: complete diffusion control of the cathodic reaction and the "activation" model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode<sup>53</sup>. The larger peaks were used to calculate the corrosion current density  $(i_{corr})$ , the Tafel slopes  $(\beta_a$  and  $\beta_c)$  and the causality factors (CF-2 and CF-3). These electrochemical parameters were simultaneously determined by Gamry EFM140 software, and recorded in Table-6. The data obviously show that, the addition of testing compound at a given concentration to the acidic solution decreases the corrosion current density, indicating that the Amoxicillin inhibit the corrosion of SS 304 in 2M HCl through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measurement data are real and of

good quality<sup>54</sup>. The inhibition efficiencies (% IE <sub>EFM</sub>) increase by increasing the concentration of Amoxicillin which calculated and recorded in **Table-6**.

**Table 6:** Electrochemical kinetic parameters obtained by EFM technique for SS 304 in M HCl without and with various concentrations of Amoxicillin at 25°C

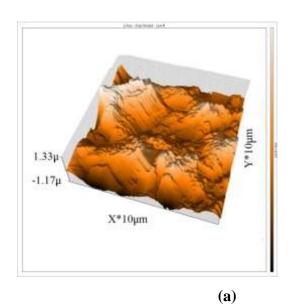
Comp.	Conc.	i <sub>corr.</sub>	$\beta_a  mV dec^-$	-β <sub>c</sub>	CF	CF	CR	Θ	%IE
	ppm	μAcm <sup>-2</sup>	1	mVdec <sup>-1</sup>	(2)	(3)	mpy		
Blank	0.0	777	105	126	1.8	2.9	355		
	50	155	75	98	1.9	2.9	115	0.801	80.1
lin	100	144	82	89	2.1	3.0	110	0.815	81.5
ici]	150	137	75	99	2.1	2.8	103	0.824	82.4
YOU	200	122	79	93	1.9	2.9	95	0.843	84.3
Amoxicillin	250	98	73	91	1.9	2.8	79	0.874	87.4
,	300	76	77	88	1.8	3.1	37	0.902	90.2

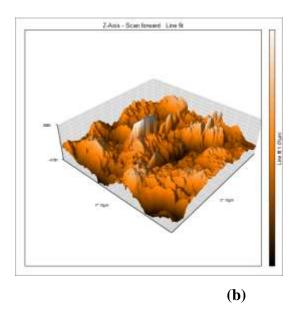


**Figure 9**. EFM for meal in 2M HCl unlucky deficiency and vicinity of distinctive convergences of amoxicillin

3. 5- Atomic force microscopy (AFM): AFM is a powerful tool to investigate the surface morphology of various samples at nano- micro scale that is currently used to study the influence of corrosion inhibitors on

metal solution interface. From the analysis, it can be gained regarding the roughness on the surface. The roughness profile values play an important role in identifying and report the efficiency of the inhibitor under study. Among the roughness take a role in explanation about the nature of the adsorbed film on the surface<sup>55</sup>. **Figure -10**, shows the 3D images as well as elevation profiles of polished of SS 304 in the absence and presence Amoxicillin as an inhibitor. It observed in **Figure-10**, the surface of SS 304 specimen (a) exposed to corroded solution affected values structure with large and deep crack, but the surface (b) reveal that is covering film adsorbed on the metal surface. The conclusion, that the adsorption film can protect the surface of the metal from corrosion process. Analysis of the values indicated higher the values of roughness parameter reached. The mean roughness are found to be (382 nm) for the blank in acid solution which placed in 2M HCl one day and analyzed. The observation of the metal surface which immersed in 2M HCl in the presence of 300 ppm of Amoxicillin inhibitor possess roughness (111 nm) compared to the blank solution. It can be noted that the value is lower than that of the blank value. The decrease in the roughness value reflected the adsorption of inhibitor molecule on metal surface, thereby reducing the rate of corrosion.

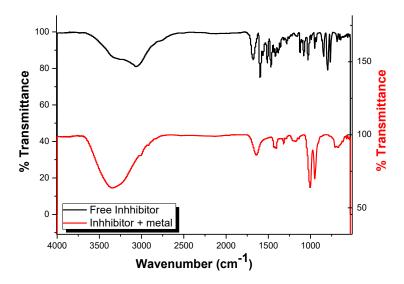




**Figure 10:** The 3D of optical images of AFM in absence (a) and presence (b) of Amoxicillin inhibitor.

3. 6- AFTIR analysis: FTIR spectroscopy displays interesting features such as high signal to noise ratio, high sensitivity and selectivity, accuracy, mechanical simplicity, short analysis time and small amount of sample required for the analysis. Figure-11 shows the FTIR spectra of the Amoxicillin inhibitor. The N-H bend at 1621 cm<sup>-1</sup> was deviation to 1551 cm<sup>-1</sup>, the C=O stretching of amide frequency has shifted from 1690 cm<sup>-1</sup> to 1638 cm<sup>-1</sup>. Indicating that there is reaction among the inhibitor and SS 304 surface. The Shifted frequencies identify the bond between the Amoxicillin and SS 304 surface. These shifts would have been caused by the decrease in electron density of N-H, C-N bond and C=O bond due to shift of electron cloud density from N and O to Fe<sup>2+</sup>. Shifts in N-H stretching frequencies are due to the hydrogen bonding. A broadband in the range 3129 to 3495 cm<sup>-1</sup>(O-H stretch) indicates the presence of coordinated/lattice water molecules formed on the cathodic sites of the metal surface

.



**Figure 11:** IR spectrum of pure Amoxicillin at 25 °C

3.7. Inhibition mode of action: We noted the formation of a film which is distributed in a random way on the whole surface of the SS 304. Due to the adsorption of the drug molecules on the metal surface and block the active site present on the surface. Also may be due to the involvement of drug molecules in the interaction with the reaction sites of SS 304 surface, lead to a decrease in the contact between SS 304 and the aggressive medium (2 M HCl) and hence, exhibited excellent inhibition effect<sup>56</sup>. This compound can be adsorbed on the metal surface through the lone pair of electrons of nitrogen, oxygen atoms and delocalized  $\pi$ -electrons of heterocyclic ring. The %IE of this investigated compound can be explained on the basis of his molecular structure. Amoxicillin, Contains eight active centers (5 O atoms and 3 N atoms) and this compound lies flat on the SS 304 surface, so, more surface area was covered and hence, more IE was observed. Other mode of adsorption is the electrostatic interaction between the negatively charged SS 304 surface<sup>57</sup> and the protonated drug molecule in acidic medium.

#### 4. CONCLUSIONS

The tested drug establish a very good inhibition for SS 304 corrosion in HCl solution, where IE% increased by increasing in Amoxicillin concentration. The decrease in corrosion inhibition with increasing temperature indicates that desorption of the adsorbed inhibitor Amoxicillin molecules takes place. Amoxicillin inhibits SS 304 corrosion by adsorption on its surface and follow Langmuir adsorption isotherm. Polarization curves show that Amoxicillin is mixed-type inhibitor. Double layer capacitances ( $C_{\rm dl}$ ) decrease with increasing the inhibitor concentration added. While the charge-transfer resistance ( $R_{\rm ct}$ ) increases. The values of inhibition efficiencies obtained from the different techniques used are compatible with each.

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